Magnesia doped Ag/Al$_2$O$_3$ – Sulfur tolerant catalyst for low temperature HC-SCR of NO$_x$

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ABSTRACT

A series of magnesia doped Ag/Al$_2$O$_3$ catalysts were prepared by modified impregnation method using boehmite as alumina precursor. The prepared catalysts were characterized and tested for the SCR of NO$_x$ using propene as reductant under lean condition. Doping of magnesia improved the low temperature catalytic activity for HC-SCR of NO$_x$ as well as sulfur tolerance. Maximum 98% NO conversion with 100% selectivity for N$_2$ was obtained at 350 °C with 7% Mg doping to Ag/Al$_2$O$_3$. The improvement in low temperature activity and the sulfur tolerance has been correlated to decreased acidity after addition of magnesia to alumina support. In situ FTIR study showed that the deactivation in the presence of SO$_2$ was due to the sulfation of silver and aluminum sites in Ag/Al$_2$O$_3$ catalyst, however its formation was suppressed in case of magnesia doped Ag/Al$_2$O$_3$ improving its sulfur tolerance.

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1. Introduction

Automobiles with diesel engines are becoming more and more popular because of their better fuel efficiency and lower CO$_2$ emission compared to their stoichiometric spark ignited gasoline counterpart. The three way catalyst which simultaneously convert NO$_x$, CO and HCs into N$_2$, CO$_2$ and H$_2$O from the exhaust of stoichiometric spark ignited gasoline engines are not capable of reducing NO$_x$ from the exhaust of lean burn engines because of excess of oxygen [1]. Thus, removal of NO$_x$ from the exhaust of lean-burn diesel engines is a major challenge. Therefore worldwide lots of efforts are being taken both in academic and industrial laboratories to develop suitable catalyst for the reduction of NO$_x$ under lean condition. There are mainly two catalytic processes being investigated for the removal of NO$_x$ under lean conditions viz.; NO$_x$ storage reduction (NSR) developed by Toyota [2,3] and selective catalytic reduction by NH$_3$ (urea) [4] or hydrocarbon as reductant (HC-SCR) [5]. In this context, HC-SCR seems to be a promising catalytic process for the removal of NO$_x$ under lean conditions since this method exploits unburned hydrocarbons already present in the exhaust gas stream. Precious metal-based catalysts (PGM), especially Pt based catalysts

such as Pt/Al$_2$O$_3$ exhibit the low temperature activity (lower than 300 °C) and are more resistant to water vapor and SO$_x$ poisoning [6]. However Pt/Al$_2$O$_3$ has two major disadvantages: low selectivity for N$_2$ (substantial amount of N$_2$O is formed) and narrow temperature window of operation for NO reduction [7,8]. Metal oxide-based catalysts, for example Al$_2$O$_3$, TiO$_2$, ZrO$_2$, MgO and these oxides promoted by various metals/metal oxides like Co, Bi, Ni, Cu, Fe, Sn, Ga, In, Au, Ag have been reported to be active for HC-SCR [9–13]. Amongst these, Ag/Al$_2$O$_3$ was found to be the most promising catalyst for practical use since it exhibits high activity for NO reduction, high selectivity for N$_2$, moderate tolerance for sulfur and water vapor, especially at higher temperatures [8]. However the major drawback of this system is the low activity and poor sulfur tolerance at low temperatures (573–673 K) due to the formation of silver and aluminum sulfate [14]. Thus improvement in the low temperature activity and sulfur tolerance in the temperature range 573–673 K is still a major challenge for HC-SCR.

One way of improving the low temperature activity and the sulfur tolerance of Ag/Al$_2$O$_3$ catalyst is by modification of the Al$_2$O$_3$ support. Previously we have demonstrated modification of alumina support by Si and Ti [15] for improved sulfur tolerance. Improvement in catalytic activity of Ag/Al$_2$O$_3$ by addition of magnesia to γ-Al$_2$O$_3$ has been reported for HC-SCR using various reductants like propene or mixture of propene and hydrogen [16,17]. Improvement in propene SCR activity of 3%Ag/Al$_2$O$_3$ after addition of magnesia has been reported by Anil Kumar et al. [16] and improvement in the activity has been correlated to the MgAl$_2$O$_4$ spinel

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formation. In continuation of our efforts to further improve the catalytic activity of Ag/Al$_2$O$_3$, we have modified the alumina support with magnesia addition by modifying the synthesis procedure to obtain uniform dispersion of MgO and subsequently of Ag and the results are reported in the present paper.

2. Experimental

2.1. Materials

Commercially available boehmite (AlOOH) was used as a precursor for γ-Al$_2$O$_3$. Magnesium nitrate [Mg(NO$_3$)$_2$·6H$_2$O] and silver nitrate (AgNO$_3$) of analytical grade were purchased from Merck and used without further purification.

2.2. Catalyst preparation

The series of 2% Ag–Mg/Al$_2$O$_3$ catalysts were prepared by varying the wt% loading of magnesia as Mg from 5% to 17% by impregnation method using boehmite (AlOOH) as Al$_2$O$_3$ precursor. In a typical preparation of the catalyst containing 5 wt% Mg, 5.3 g magnesium nitrate [Mg(NO$_3$)$_2$·6H$_2$O] was dissolved in 50 mL distilled water. To this solution boehmite (13.08 g) was added under constant stirring. The slurry was evaporated followed by overnight drying at 373 K and then calcination at 773 K for 6 h. To this calcined sample aqueous silver nitrate solution (0.314 g) corresponding to 2 wt% loading was added. Water from the slurry was removed by heating on a hot plate with constant stirring at 343 K. The sample was dried overnight at 373 K followed by calcination in air at 873 K for 6 h. The final sample was labeled as Ag5MgAl, where 5 denote the wt% loading of Mg. The above procedure was repeated for the preparation of the samples with various loading of Mg as 7%, 10%, and 17% and the samples were labeled as Ag7MgAl, Ag10MgAl and Ag17MgAl, respectively. For comparison, 2% Ag/Al$_2$O$_3$ catalyst (labeled as AgAl) was prepared by impregnation method using aqueous silver nitrate solution and boehmite as a silver and alumina precursors respectively. The aqueous solution of silver nitrate was added to slurry of boehmite in water with constant stirring. The slurry was evaporated followed by overnight drying at 373 K and calcination in air at 873 K for 6 h.

2.3. Catalyst characterization

2.3.1. Powder X-ray diffraction studies
The powder X-ray diffraction data was collected on a Rigaku Miniflex diffractometer equipped with a Ni filtered Cu Kα radiation (λ = 1.5406 Å, 30 kV, 15 mA). The data was collected in the 2θ range 20–80° with a step size of 0.02° and scan rate of 4° min^{-1}.

2.3.2. Nitrogen adsorption studies
The BET surface area of the calcined samples was determined by N$_2$ sorption at 77 K using NOVA 1200 (Quanta Chrome) equipment. Prior to N$_2$ adsorption, the material was evacuated at 573 K under vacuum. The specific surface area, S_{BET}, was determined according to the BET equation.

2.3.3. NH$_3$ temperature programmed desorption (TPD) study
The NH$_3$-TPD experiments were performed using a Micromeritics Autochem 2910 instrument. A weighed amount of the sample (≈100 mg) was placed in a quartz reactor, pretreated in a flow of He gas at 773 K for 1 h (ramp rate of 10 K min^{-1}) and cooled to 373 K. The catalyst was then exposed to a gas mixture of NH$_3$ (5% NH$_3$–95% He, 50 mL min^{-1}) at 373 K, followed by evacuation at 373 K for 3 h. Then, the measurement was made from 373 K to 973 K with a heating rate of 5 K min^{-1} in flowing He as a carrier gas at a flow rate of 60 mL min^{-1} until ammonia was desorbed completely. A thermal

conductivity detector (TCD) was employed at the outlet of the reactor to measure the volume of ammonia consumed during reduction of the samples.

2.3.4. UV–vis diffuse reflectance spectra
UV–vis diffuse reflectance spectra was recorded using Perkin Elmer Lambda 650 as neat sample for comparison of different silver species formed in AgAl and Ag7MgAl.

2.3.5. X-ray photoelectron spectroscopy study
X-ray photoelectron spectroscopy (XPS) was used for the characterization of surface of fresh catalysts. XPS experiments were performed using a ESCA 3000 spectrometer equipped with an magnesium source for excitation in the analysis chamber under ultra high vacuum (10^{-10} Torr). Binding energy (B.E.) values were referenced to the binding energy of the Al 2p core level (74.6 eV).

2.4. Catalytic activity measurement

The SCR of NO using propene as reductant was carried out at atmospheric pressure in a quartz tubular down flow reactor (inner diameter 4 mm). A mechanical mixture of catalyst powder (500 mg, particle size <180 μm) and commercial silica gel (2.0 g, particle size 125–250 μm) was placed in the reactor and a thermocouple was inserted in the center of the catalyst bed to measure the temperature. Prior to the reaction catalyst was activated at 773 K for 1 h in 10% O$_2$/He flow. The typical reactant gas mixture consisting of NO (1000 ppm), C$_3$H$_6$ (2000 ppm), CO$_2$ (10%), O$_2$ (5%), 0 or 20 ppm SO$_2$, 0 or 9% H$_2$O and balance helium were fed from independent mass flow controllers. The online analysis of the effluent gases was carried out by monitoring the relative masses m/z = 30 (NO), 28 (N$_2$, CO), 44 (N$_2$O, CO$_2$), and 41 (C$_3$H$_6$) as function of time using a quadrupole mass spectrometer (Hiden Analytical HPR 20), a chemiluminescence NO/NO$_2$/NO$_x$ analyzer (42C HL, Thermo Environmental) and a micro GC (Agilent 3000 A) equipped with a molecular sieve 5 Å column. The reaction was carried out at a gas hourly space velocity (GHSV) of 20,000 h^{-1} (W/F = 0.05 g h L^{-1}). In these studies NO and C$_3$H$_6$ conversions were calculated as follows:

$$NO\,conversion\,(\%) = \frac{[NO_x]_{inlet} - [NO_x]_{outlet}}{[NO_x]_{inlet}} \times 100$$

$$C_3H_6\,conversion\,(\%) = \frac{[C_3H_6]_{inlet} - [C_3H_6]_{outlet}}{[C_3H_6]_{inlet}} \times 100$$

2.5. In situ diffuse reflectance FT-IR study (DRIFTS)

The diffuse reflectance FT-IR measurements were carried out under a flow of He in a high temperature cell (Spectra-Tech) fitted with a Zn–Se window using Shimadzu 8000 FT-IR spectrometer. The temperature in the cell was varied from 303 to 698 K. About 30 mg finely crushed sample was placed in a sample holder and pretreated at 698 K for 2 h in 10% O$_2$/He flow to remove adsorbed moisture. The spectrum of neat catalyst was recorded (400 scans with resolution 4 cm^{-1}) at 623 K prior to the experiment under He flow. The SCR gas mixture (1000 ppm NO, 2000 ppm C$_3$H$_6$, 10% CO$_2$, 5% O$_2$ and 0 or 20 ppm SO$_2$ with He balance) was passed on the catalyst surface and evaluation of different species on the catalyst surface were monitored with time. The reported spectra are difference spectra of adsorbed species and neat catalyst.

3. Results and discussion

The magnesia doped catalysts were prepared by modified impregnation method. Boehmite was used as an alumina
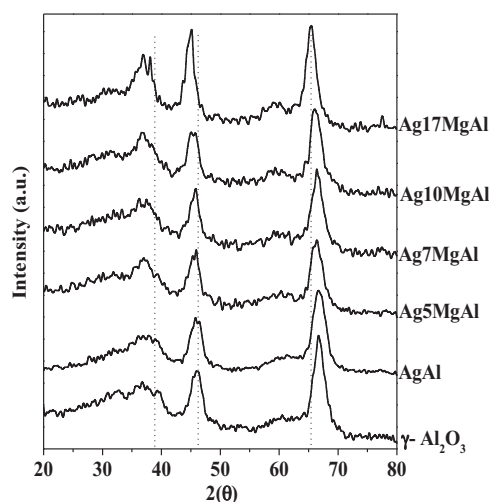
Fig. 1. X-ray diffraction pattern of fresh γ-Al$_2$O$_3$ and the different magnesia modified Ag/Al$_2$O$_3$ samples.

Fig. 2. Comparison of UV–vis diffuse reflectance spectra of AgAl and Ag7MgAl.

precursor on which various loadings of magnesia (5–17 wt% as Mg) were impregnated. Silver (2 wt%) was impregnated on calcined Mg–Al$_2$O$_3$ to get the final AgMgAl catalysts after calcination. The catalysts were characterized by various physico-chemical methods.

Fig. 1 shows the XRD patterns of the series of catalysts prepared along with XRD of γ-Al$_2$O$_3$ for comparison. Incorporation of Ag in all the samples did not show any separate phase of metallic Ag or Ag$_2$O species indicating high dispersion of Ag on the support as well as amorphous nature due to low silver loading (2 wt% Ag).

For AgAl sample, only the diffraction lines for γ-Al$_2$O$_3$ phase at $2\theta = 36.7°$, $46.0°$ and $66.90°$ (JCPDS: 29-0063) were observed. In case of magnesia modified samples, similar trend was seen up to Ag7MgAl. Further increase in the Mg content (10 and 17 wt%) has resulted in the shift in the peaks at $46.0°$ and $66.90°$ to $45.10°$ and $65.35°$, respectively. This shift may be attributed to increase in catalyst particle size with higher doping of magnesia to γ-Al$_2$O$_3$. Since crystalline MgO in cubic phase shows diffraction peaks at $43.1°$ coincide with the peak at $43.7°$, it is difficult to comment on existence of separate MgO phase. Alumina modification by Mg from 5% to 17% did not show formation of magnesium aluminate (MgAl$_2$O$_4$) phase at all the loadings as reported by Anil Kumar et al. [16].

Table 1 shows the BET surface area of γ-Al$_2$O$_3$, AgAl and AgMgAl samples prepared in this study. Addition of Ag to the γ-Al$_2$O$_3$ support has led to the decrease in the surface area from 237 to 216 m^2 g^{-1}. In case of Mg modified silver alumina catalysts, with increase in the Mg content from 5% in case of Ag5MgAl to 17% in case of Ag17MgAl decrease in the surface area was observed from 169 to 111 m^2 g^{-1}.

The total acidity of the samples measured by temperature programmed desorption of NH$_3$ is shown in Table 1. Pure γ-Al$_2$O$_3$ showed the highest acidity (0.714 mmol g^{-1}) amongst all the samples. Addition of 2 wt% Ag onto the support led to the decrease in the total acidity of the support to 0.615 mmol g^{-1}. Mg loaded samples showed further decreased in the acidity with increase in Mg

loading due to basic nature of MgO [18,19]. The acidity decreased from 0.550 mmol g^{-1} for Ag5MgAl to 0.412 mmol g^{-1} for Ag17MgAl (Table 1).

Fig. 2 shows UV–vis diffuse reflectance spectra of the AgAl and Ag7MgAl catalysts. Both the catalysts showed band below 400 nm indicating highly uniform distribution of silver species on the surface. This broad band in the range of 200–400 nm showed presence of three maxima, first maxima at 225 nm assigned to Ag$^+$ ions, second maxima at 260–320 nm assigned to Ag$_n^{\delta+}$ clusters and third maxima at 350 nm due to metallic Ag [16]. When relative intensities of the three bands in AgAl and Ag7MgAl were compared, the Ag$_n^{\delta+}$ band was more prominent in case of Ag7MgAl compared to AgAl. The band at 350 nm was very small in case of Ag7MgAl compared to AgAl indicating low concentration of metallic Ag on the surface of Ag7MgAl.

Fig. 3 shows XPS spectra of Ag7MgAl and AgAl catalyst. Both the catalysts showed peaks at binding energy 367.1 and 368.6 eV corresponding to Ag$^+$ and Ag^o species, respectively [16]. A new peak was observed (small shoulder) at binding energy 367.7 eV which may be due to Ag$_n^{\delta+}$ species. When ratio of intensities for peak at 368.6 eV (Ag$^+$) and at 367.7 eV (Ag$_n^{\delta+}$) is considered the ratio is much higher for Ag7MgAl compared to AgAl, which may be due to

Table 1
Specific surface area and total acidity of the catalysts.

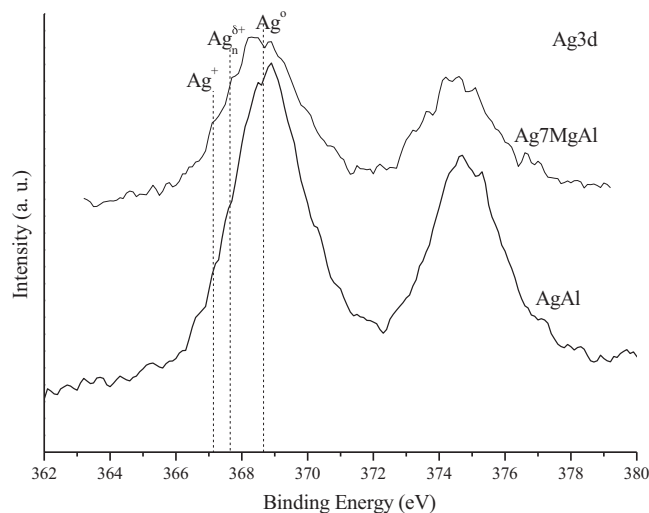| Samples	Surface area (m^2 g^{-1})	Total acidity (mmol g^{-1})
γ-Al$_2$O$_3$	237	0.714
AgAl	216	0.615
Ag5MgAl	169	0.550
Ag7MgAl	166	0.527
Ag10MgAl	157	0.483
Ag17MgAl	111	0.412

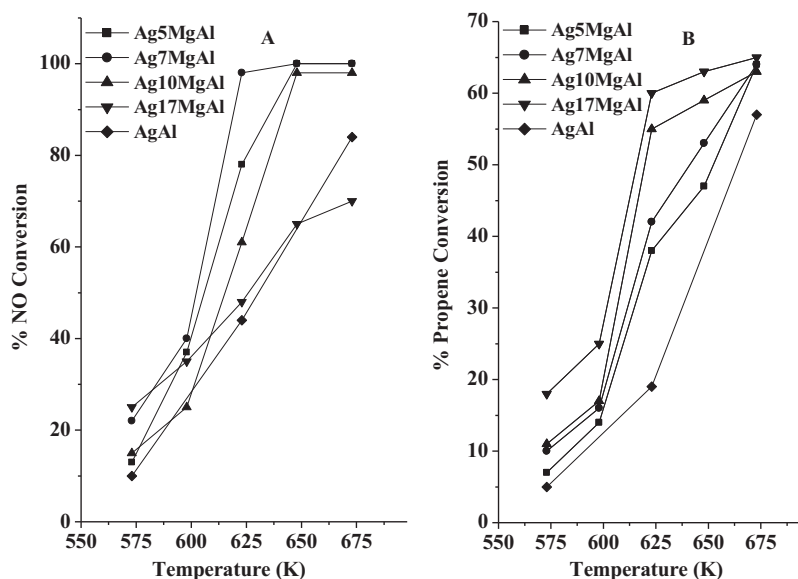**Fig. 3.** Comparison of XPS spectra of Ag7MgAl and AgAl samples.

Fig. 4. NO conversion (A) and C_3H_6 conversion (B) over AgAl and AgMgAl samples as a function of temperature. Reaction conditions: 1000 ppm NO, 2000 ppm C_3H_6, 5% O_2, 10% CO_2, He balance, GHSV = 20,000 h^{-1}.

the presence of more number of $Ag_n^{\delta+}$ species in Ag7MgAl. The XPS results are in good agreement with UV–vis results.

3.1. Catalytic activity study

The catalytic activity of AgAl and AgMgAl with different Mg content was tested for SCR of NO_x using propene in the absence and presence of SO_2.

3.2. Catalytic performance of AgMgAl and AgAl

The temperature dependent SCR activity of NO using C_3H_6 as reductant in the temperature range of 573–673 K for AgAl and AgMgAl samples is shown in Fig. 4. At 573 K the NO conversions (Fig. 4A) were found to be very low in the range of 7–25% with the lowest conversion for AgAl (7%) and the highest conversion for Ag17MgAl (25%). However with gradual increase in the temperature to 623 K, Ag7MgAl showed the highest NO conversion (98%) among all the catalysts under study specially compared to AgAl which showed only 44% NO conversion. The highest catalytic activity of Ag7MgAl at 623 K can be correlated to low propene (42%) conversion (Fig. 4B) which clearly indicates minimum direct oxidation of propene, making propene available for reduction of NO. In all the Mg doped catalysts very high propene efficiency for NO reduction was observed due to low direct HC oxidation. Previous reports on Ag/Al_2O_3 catalysts [20] revealed that the presence of larger silver particles at higher Ag loadings resulted in low NO reduction due to complete direct oxidation of C_3H_6. High oxidizing nature of the catalyst at high Ag loading results in non-availability of hydrocarbon for reduction of NO_x, leading to decrease in SCR activity. High propene efficiency for NO_x reduction of Ag7MgAl can be correlated to smaller silver particle compared to AgAl. The catalytic activity of Ag7MgAl for HC-SCR of NO was higher compared to previously reported results by Anil Kumar et al. [16] using 3% Ag/MgAl system which was correlated to the formation of $MgAl_2O_4$ spinel structure. However in the present study the formation of $MgAl_2O_4$ spinel phase was not observed at all the Mg loadings, may be due to the modified synthetic procedure. Due to loading of 3% Ag on MgAl in case of previous studies, very high propene oxidation was observed compared to 2% Ag loading in present study. The high catalytic activity of Ag7MgAl can be attributed to the formation of more

$Ag_n^{\delta+}$ clusters on the catalyst surface as observed in UV–vis (Fig. 2) which is reported to be more active for NO reduction [16,21,22]. When product selectivity was monitored for all the catalysts over the complete temperature range, it was observed that nitrogen was the only product formed with 100% selectivity without any undesired byproduct formation like NO_2 and N_2O. It can be seen that the modification of the alumina support with MgO has improved the low temperature activity compared to AgAl as well as it has improved the hydrocarbon efficiency for NO reduction compared to direct hydrocarbon oxidation.

3.3. Catalytic performance of AgAl and AgMgAl in the presence of SO_2

The effect of SO_2 addition in the reaction feed on the catalytic activity as a function of time-on-stream was monitored under dry conditions at 623 K, using Ag7MgAl catalyst as it showed the best SCR activity at this temperature. First the catalyst was exposed to a reaction mixture containing 1000 ppm NO + 2000 ppm C_3H_6 + 5% O_2 + 10% CO_2 for 60 min. After attaining the steady state NO conversion, 20 ppm SO_2 was introduced in the feed and NO conversion was measured with time on stream (Fig. 5). In the absence of SO_2, AgAl showed 44% NO conversion which decreases to 21% in the presence of 20 ppm SO_2. On the other hand, upon exposure to 20 ppm SO_2 the NO conversion over Ag7MgAl decreased marginally from 98% to 90%. From this result it is seen that in case of AgAl the decrease in catalytic activity was about 50% whereas in case of Ag7MgAl the decrease in catalytic activity was marginal. The addition of magnesia to alumina has considerably improved the low temperature activity as well as sulfur tolerance. The improvement in sulfur tolerance after addition of alkali metals has been previously reported by Rao et al. [23,24]. The addition of alkali metals have shown to suppress the accumulation of SO_2 on the AgAl. Hence in present case also addition of magnesia may suppress the SO_2 accumulation leading to significant sulfur tolerance of the AgMgAl catalysts.

3.4. Catalytic performance of Ag7MgAl in the presence of water

The effect of addition of water (9%) in the reaction feed was studied for Ag7MgAl (Fig. 6) at 623 K. The results clearly showed the decrease in NO conversion from 98% to 57% with corresponding
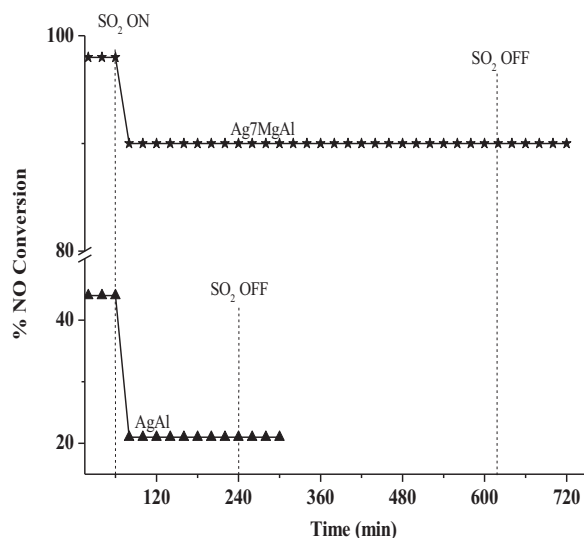
Fig. 5. Comparative study of SO_2 tolerance of AgAl and Ag7MgAl as a function of time. Reaction conditions: 1000 ppm NO, 2000 ppm C_3H_6, 5% O_2, 10% CO_2, 20 ppm SO_2, He balance, GHSV = 20,000 h^{-1}, 623 K.

decrease in propene conversion from 42% to 28% after addition of water. However this deactivation was reversible or temporary and NO as well as propene conversion regained its original value which was observed in repeated cycles in presence and absence of water. This clearly indicated the physisorption of water on the catalyst surface leading to non-accessibility of catalytically active sites to NO and C_3H_6 [25]. However when water was removed from the feed the physisorbed water gets desorbed making the catalytically active sites accessible to the reactants (NO + C_3H_6).

3.5. Catalytic performance of Ag7MgAl in the presence of SO_2 and water

The effect of addition of SO_2 and water separately showed marginal decrease in NO conversion in presence of SO_2 whereas reversible decrease in conversion in presence of water. Hence the combined effect of mixture of SO_2 and water on NO and C_3H_6 conversion was studied in presence of 20 ppm SO_2 and 9% water (Fig. 7) at 623 K. The results showed decrease in NO conversion from 98% to 60% with corresponding decrease in C_3H_6 conversion
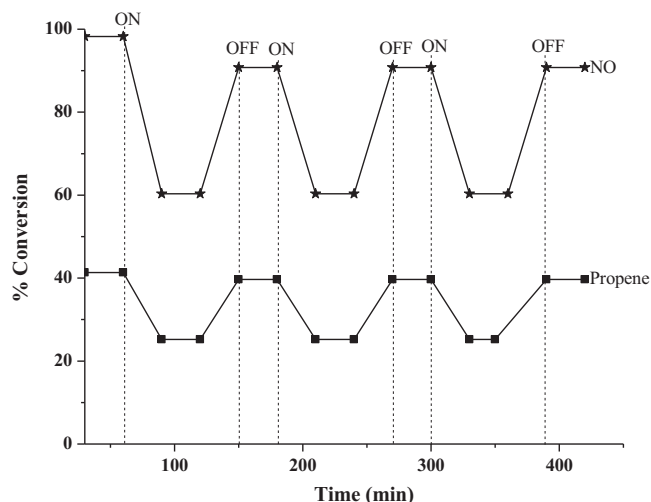

Fig. 6. Effect of H_2O addition on catalytic activity of Ag7MgAl as a function of time. Reaction conditions: ON: 1000 ppm NO, 2000 ppm C_3H_6, 5% O_2, 10% CO_2, 9% H_2O, He balance, OFF: 1000 ppm NO, 2000 ppm C_3H_6, 5% O_2, 10% CO_2, GHSV = 20,000 h^{-1}, 623 K.

Fig. 7. Effect of SO_2 + H_2O addition on catalytic activity of Ag7MgAl as a function of time. Reaction conditions: GHSV = 20,000 h^{-1}, temperature 623 K. ON: 1000 ppm NO, 2000 ppm C_3H_6, 5% O_2, 10% CO_2, 9% H_2O, 20 ppm SO_2 He balance. OFF: 1000 ppm NO, 2000 ppm C_3H_6, 5% O_2, 10% CO_2, 9% H_2O.

from 42% to 25% after addition of SO_2 and water together. However after removal of SO_2 and water from the feed the activity was not regained completely. There was marginal decrease in NO conversion from 98% to 92% with no decrease in propene conversion (42%). However it was interesting to note that when again SO_2 + H_2O was added to reaction feed the activity was completely regained to 92% for NO and 42% for C_3H_6 conversions. This clearly indicates that the marginal catalyst deactivation takes place due to SO_2 only in first cycle and in subsequent cycles reversible deactivation was observed due to SO_2 + water.

The above results have clearly indicated that addition of MgO to alumina has considerably improved the low temperature activity as well as sulfur tolerance. These results are superior to the work previously reported by Anil Kumar et al. [16] on similar composition however using 3% Ag loading on MgAl. There was only moderate increase in NO conversion observed from 83% for 3AgAl (3 wt% Ag/Al_2O_3) to 95% after addition of optimum Mg (5 wt%) to 3%AgAl at 623 K compared to present results where large increase in NO conversion was observed from 44% for AgAl to 98% for Ag7MgAl with 2% Ag loading. When sulfur tolerance was compared, the present catalyst has shown much higher sulfur tolerance (NO conversion decreased marginally from 98% to 90%) compared to AgAl where NO conversion decreased from 44% to 21%. The high sulfur tolerance as well as large improvement in the low temperature activity (623 K) in case of Ag7MgAl and AgAl compared to previously reported Ag5MgAl and 3AgAl can be attributed to the catalyst synthetic procedure as well as lower Ag loading (2%). The importance of surface acid–base property in hydrocarbon activation and NO reduction has been emphasized by many researchers [26–30]. In present case also lower loading of Ag as well as reduced acidity of the catalyst after Mg doping has led to the high efficiency of propene for NO reduction and not much direct propene oxidation was observed. Also it is worth mentioning that in present work 100% selectivity for N_2 was obtained under entire range of reaction conditions for all the catalysts whereas in case of previous work by Anil Kumar et al., 2–5% selectivity for N_2O was observed at higher temperatures. When the present results are compared with our previous results [15] using AgAl modified with Si or Ti, considerable improvement in low temperature activity for NO conversion was obtained by Mg modification. However sulfur tolerance was excellent (no deactivation) in case of Si or Ti modification compared to present work. This excellent sulfur tolerance in case of Si or Ti modification was
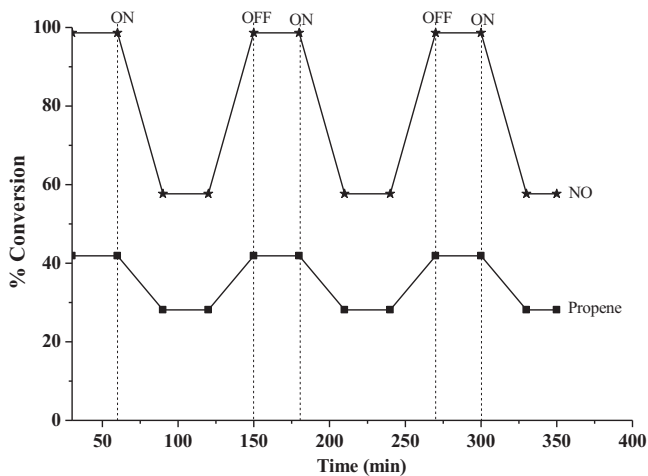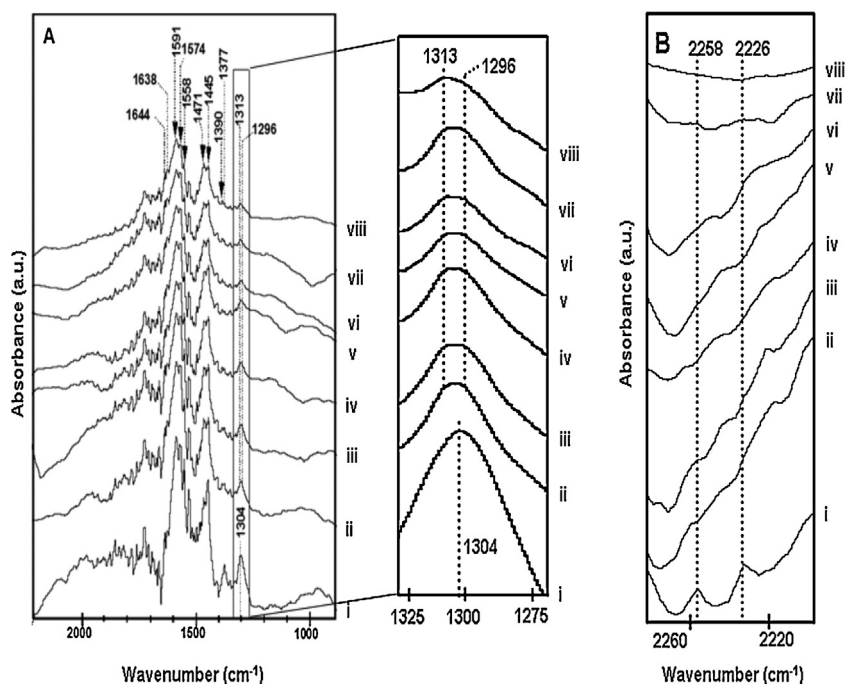
Fig. 8. Dynamic changes of in situ DRIFTS spectra over AgAl during the SCR of NO in presence of SO$_2$ at 623 K. (i) NO + C$_3$H$_6$ – 60 min, (ii) NO + C$_3$H$_6$ + SO$_2$ – 10, iii) 30, (iv) 60, (v) 120, (vi) 180 (vii) 240 and (viii) 300 min. Gas composition: 1000 ppm NO, 2000 ppm C$_3$H$_6$, 5% O$_2$, 10% CO$_2$, 20 ppm SO$_2$, He balance.

attributed to increase in acidity compared to AgAl whereas after modification with Mg in present work the acidity has decreased compared to AgAl.

3.6. In situ DRIFTS study

To examine the mechanistic aspect of catalyst deactivation in presence of SO$_2$, in situ FT-IR studies were carried out in the absence of water at 623 K. Since the deactivation due to SO$_2$ was more prominent at 623 K. Two sets of experiments were carried out for each catalyst. In the first experiment, standard SCR gas mixture (1000 ppm NO + 2000 ppm C$_3$H$_6$ + 10% CO$_2$ + 5% O$_2$) was passed over the catalyst at 623 K and the species formed were monitored as a function of time. In second experiment along with standard SCR mixture, 20 ppm SO$_2$ was introduced in the feed at 623 K and the formation of different species was monitored as a function of time
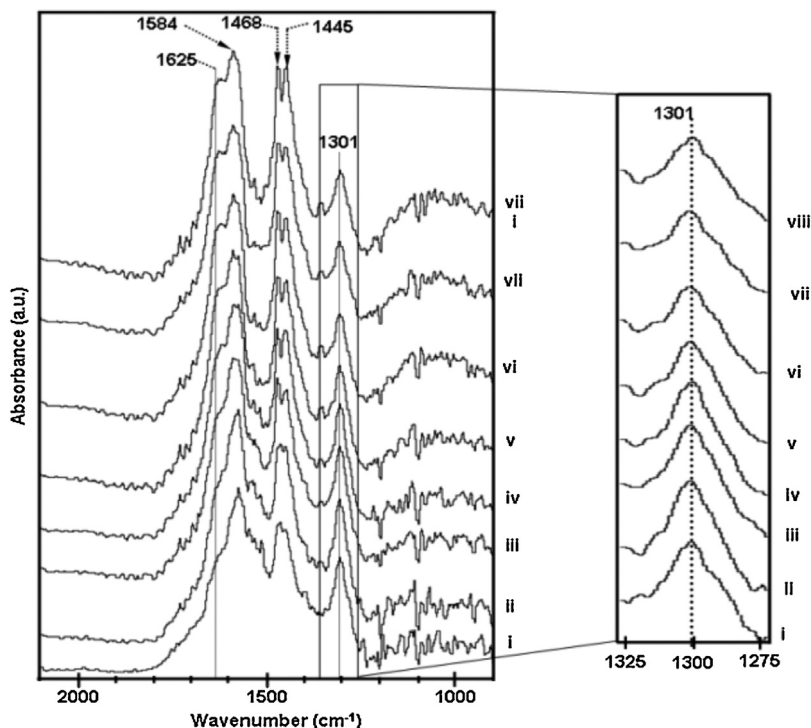

Fig. 9. Dynamic changes of in situ DRIFTS spectra over Ag7MgAl during the SCR of NO in presence of SO$_2$ at 623 K. (i) NO + C$_3$H$_6$ – 60 min, (ii) NO + C$_3$H$_6$ + SO$_2$ – 10, (iii) 30, (iv) 60, (v) 120, (vi) 180 (vii) 240 and (viii) 300 min. Gas composition: 1000 ppm NO, 2000 ppm C$_3$H$_6$, 5% O$_2$, 10% CO$_2$, 20 ppm SO$_2$, He balance.

Table 2
Assignments of IR bands formed on AgAl and Ag7MgAl during in situ studies.

Wavenumber (cm^{-1})	Surface species	Vibrations	Observed wavenumber (cm^{-1})	References
1585	Carboxylate COO$^-$	ν^a_{OCO}	1586	[20]
1460		ν^s_{OCO}	1456 and 1471	
1595	Formate HCOO$^-$	ν^a_{OCO}	1591	[20]
1380		ν^s_{OCO}	1377	
1390		δ_{CH}	1390	
1550	Monodentate nitrate NO$_3^-$	$\nu_{N=O}$	1558	[20]
1250		ν^a_{ONO}	Not detected	
1590	Bidentate nitrate NO$_3^-$	$\nu_{N=O}$	1595	[20]
1305		ν^a_{ONO}	1304, 1301	[20]
1560	Ad-NO$_x$		1558	[20]
1313	Ag$_2$SO$_4$		1313	[34]
1384	Al(SO$_4$)$_3$		Not detected	[32]
1637	H$_2$C=CH—O—M		1644	[32]
2230	Ag-NCO		2226	[32]
2260	Al-NCO		2258	[32]

(s = symmetric, a = asymmetric and δ = bending).

and the results are shown in Figs. 8 and 9, respectively. Spectrum of AgAl [as shown in Fig. 8A(i)] was taken as reference. Based on previous literature data [20,31,32], IR bands assigned to the different intermediates are summarized in Table 2.

For AgAl catalysts in absence of SO$_2$ [Fig. 8A(i)] the characteristic infrared bands due to acetates (1574, 1445 and 1471 cm^{-1}), formates (1390 and 1377 cm^{-1}) and adsorbed nitrates (1638, 1591 and 1304 cm^{-1}) [32,33] were observed along with surface isocyanate species, Ag-NCO and Al-NCO (2226 and 2258 cm^{-1}) [32] as well as surface enolic species (H$_2$C=CH—O—M) (1644 cm^{-1}) [31]. Under identical reaction conditions, for Ag7MgAl these bands were observed at 1584, 1468 and 1445 cm^{-1} (acetate species), 1301 cm^{-1} (bidentate nitrate) and 1625 cm^{-1} (enolic species). Along with presence of carboxylate species [20], weak bands were also observed near 2226 cm^{-1} previously assigned to —NCO species [31,32].

The effect of SO$_2$ (20 ppm) on the interaction of propene with NO in presence of oxygen on catalyst surface and in turn on formation of different intermediates is shown in Fig. 8A(ii–viii). After introducing 20 ppm SO$_2$ in the SCR feed, very weak signal for silver sulfate species started appearing at 1313 cm^{-1} after 30 min which appeared as broadening of the peak at 1304 cm^{-1}. The intensity of the band increased from 30 to 300 min with maxima shifted from 1304 to 1313 and 1296 cm^{-1}. Corresponding decrease in intensity of Ag-NCO and Al-NCO species was observed. After exposure to SO$_2$, the previously discussed IR bands ascribed to acetates, formates and nitrates did not disappear which indicate that development of nitrates species as well as adsorbed C-containing intermediates on AgAl surface. These results indicated the sulfation of Ag phase in case of AgAl in presence of 20 ppm SO$_2$. In case of Ag7MgAl (Fig. 9) exposure to 20 ppm SO$_2$ did not show formation of Ag-sulfate at 1313 cm^{-1} even up to 300 min. The absence of formation of silver sulfate in case of Ag7MgAl proved the improved sulfur tolerance of this catalyst. It is also observed that decrease in intensity of the IR band assigned to Ag-NCO and Al-NCO on Ag7MgAl was not significant compared to AgAl which can be correlated to a lesser deactivation on Ag7MgAl than on AgAl due to SO$_2$ poisoning. The sulfation of Al$_2$O$_3$ generally evidenced by the presence of IR band at 1384 cm^{-1} (Al-sulfate) was not significantly observed even after 300 min exposure to SO$_2$, in case of both the catalysts which may be due to low concentration of SO$_2$ in the feed gas. Hence it is clear that addition of MgO to AgAl prevents formation of silver sulfate as well as aluminum sulfate as evidenced from IR leading to high sulfur tolerance of the modified catalyst.

4. Conclusions

Doping of alumina support in case of Ag/Al$_2$O$_3$ with MgO has improved the low temperature activity of the catalyst for SCR of NO using propene as reductant. Maximum NO conversion of 98% was obtained at 623 K compared to 44% for Ag/Al$_2$O$_3$. The increase in the catalytic activity upon addition of magnesia has been correlated with the decrease in the total acidity of the support. Ag7MgAl catalyst showed the highest catalytic activity at lower temperature which could be correlated to low temperature activation of C$_3$H$_6$ and presence of more Ag$_n^{\delta+}$ species, which in turn resulted in higher NO conversion. The MgO modification has also shown considerable improvement in sulfur tolerance in presence of 20 ppm SO$_2$ with marginal decrease in NO conversion from 98% to 90%. The in situ FT-IR studies have shown that formation of silver sulfate as well as aluminum sulfate is prevented after addition of MgO to AgAl which is the main reason for high sulfur tolerance.

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